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Title: **The Artifact-Free Physiochemical Characterization of Aerosol Particles During ACE-Asia**

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The Artifact-Free Physiochemical Characterization
of Aerosol Particles During ACE-Asia

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ABSTRACT

We propose to study the character and distribution of aerosol during the ACE-Asia intensive field study onboard the Research Vessel R.H. Brown. We propose to make such measurements by using a combination of the Evolved Gas (EGA) and Thermal Volatilization (TVA) techniques to determine the relative contributions of inorganic species, organic species, and elemental carbon that make up the aerosol. The advantage to the combined TV/EG system is in its ability to measure number density and size distributions of each heated stream while simultaneously collecting filter samples for analysis with EGA. Pre- and post-mission controlled laboratory experiments will yield thermographic 'signatures' of aerosol species and provide a controlled calibration/validation of both methods. Thus the combined instrument coupled with laboratory calibrations and comparisons will give a more quantified characterization of the atmospheric aerosol than has been possible in the past. Our results will be compared to a variety of complementary studies proposed for ACE-Asia. Our measurements will also be used to calculate aerosol optical properties using models developed at Ames for closure experiments with onboard radiometers and satellites.

A prerequisite for achieving a better understanding of the effects of aerosols on radiative transfer, atmospheric chemistry, and ultimately on climate is the ability to perform reliable measurements that can discriminate between organic, black carbon, and inorganic aerosols. Conventional methods rely on filter-collected samples that suffer from sampling artifacts and insufficient time resolution. The proposed approach is based on the in-situ thermal volatilization analysis (TVA) combined with the ex-situ thermal evolved gas analysis (EGA) methods which are complementary. These techniques have proven effective in discriminating aerosol composition in the past. The thermal volatility of aerosol will be used to characterize their physical chemistry. By heating to high temperatures we expect to be able to discriminate the inorganic, organic, and other refractory aerosol into compositional groups or families. Past comparisons of these methods have led to significant findings in ACE-1, ACE-2, and TARFOX. We believe that combining the methods at inception, as proposed here, will greatly improve our ability to quantify atmospheric aerosol.

During FY 2000 we will make laboratory and local surface measurements designed to help characterize the aerosol composition and calibrate the instrument. The second year, FY 2001, will be primarily devoted to integrating onto the selected platform, participating in the ACE-Asia intensive field study, making preliminary analyses of the data and comparison with other ACE-Asia participants who are attempting to determine aerosol composition. During FY 2002, final data analyses will be made, and we will use our measurements, other in situ, remote and satellite measurements and computer models to determine the chemical, physical, and optical properties of the aerosol and their effect on radiative forcing.

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1.   RESULTS FROM PREVIOUS RESEARCH

This section briefly summarizes our results from previous related projects in accordance with the submittal guidelines in the Program Announcement.

The Cloud and Microphysics Group at Ames has been measuring size distributions of aerosol and cloud for 15 years with optical sizing spectrometers and wire impactors.

Subsonic Assessment, Ozone and Nitrogen Oxide Experiment (SONEX), 1997, NASA.
Measurements were made using the TVA technique during this campaign along the north Atlantic flight corridors. These measurements confirmed the presence of a large number of small sulfuric acid droplets that are an indicator of aircraft pollution [*Ferry et al.*, 1999]. These measurements will be discussed later.

It was observed that the measured CN enhancement due to aircraft emissions was accompanied by an increase in nitrogen oxide. An emission index for CN was then calculated to be about 8×10^{17} particles per kg fuel in rough agreement with other estimates.

Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS), 1996-1998, NASA.
The group measured the proportion of sulfuric acid and carbonaceous aerosol in the stratosphere and studied their role in stratospheric photochemistry through the use of computer simulations. Hypothesized reactions involving carbonaceous aerosols in the destruction of ozone resulted in simulations that did not agree with other measurements.[*Strawa et al.*, 1999] The effect of warm stratospheric temperatures on ozone photochemistry was also explored using computer simulations.[*Drdla* et al., 1999].

Airborne Antarctic Ozone Experiment (AAOE), 1987, NASA, and
Airborne Arctic Stratospheric Expeditions (AASE I and II), 1989 and 1992, NASA.
The proportion of NO_3, Cl, and SO_4^- aerosol in the polar stratosphere was determined. The condensation temperature of nitrate was established at 196.4 K, which validated the hypothesis that inert chlorine nitrate decomposed to yield chlorine monoxide which lead to ozone depletion. [*Pueschel et al.*, 1989, 1990]

The Aerosol Group at LBL has been characterizing carbonaceous aerosol for many years. A brief summary of results from the group appear below.

TARFOX, 1997, DOE . Airborne measurements along the east coast of the US during TARFOX have demonstrated that carbon mass was, on average, 50% of the total dry aerosol mass [*Novakov et al.*, 1997].

ACE-2, 1997, DOE. The group has also made extensive measurements of the organic aerosol content in tropical trade winds and Pacific air masses [*Novakov and Penner*, 1993], shipboard collected samples during ACE-2 [*Novakov et al.*, Tellus in press],

Indian Ocean Experiment (INDOEX), 1998, DOE. Early indication are that organic aerosol make up a significant proportion of the aerosol coming from the Indian sub-continent. LBL measurements are helping to quantify these results.

2. PROPOSED RESEARCH

2.1 Scientific Rationale

Atmospheric aerosol is composed of mixtures of anthropogenic and natural chemical species, such as sulfates, nitrates, sea salt, mineral dust particles, and chemically and physically complex carbonaceous material. These aerosol play a critical role in tropospheric chemistry and in radiative transfer in the atmosphere. The ACE-Asia Survey and Evolution Component Scientific Overview (Huebert et al., 1999, called AA-SEC hereafter) describes the climate radiative forcing by aerosols as one of the most significant environmental issues of our time.

Of the species that compose most atmospheric aerosols, anthropogenic sulfate has been the subject of the most attention with respect to both direct and indirect radiative effects [*Charlson et al.*, 1992; *Taylor and Penner*, 1994; *Jones et al.*, 1994]. However, sulfate species are not the only and are often not even the dominant component, of both anthropogenic and natural submicron aerosol mass. There is growing evidence that in both remote oceanic and combustion influenced continental environments the mass concentrations of carbonaceous aerosol material is comparable to or exceeding those of sulfate. However, the experimental evidence is sketchy at best, being based on a few measurements. The fundamental importance of knowing the composition and distribution of tropospheric aerosols cannot be understated. The carbonaceous fraction of the atmospheric sub-micron aerosol is composed of two classes of materials broadly referred to as elemental or black carbon (BC) and organic carbon (OC). Black carbon is produced by incomplete combustion of fossil and biomass fuels and it is primarily responsible for light absorption. Organic carbon, the most abundant component of the carbonaceous aerosol material, is introduced into the atmosphere either directly in particulate form or by, gas-to-particle conversion of anthropogenic and biogenic precursor gases. Both BC and OC contribute to light extinction.

The importance of carbonaceous aerosols as light scatterers and absorbers has been documented in visibility degradation studies. These have shown that carbonaceous aerosols are responsible for a large part of the light extinction in urban areas [*Groblicki et al.*, 1981; *Hasan and Dzubay*, 1983; *Shah et al.*, 1984], rural areas [*Trijonis*, 1982], and remote continental areas [*Malm et al.*, 1994]. Airborne measurements off the east coast of the United States during Tropospheric Aerosol and Radiative Forcing Experiment (TARFOX) Project [*Hobbs et al.*, 1996] have demonstrated that the carbon mass was, on average, 50% of the total dry aerosol mass [*Novakov et al.*, 1997], that the carbon mass fraction increased with altitude. The TARFOX results have shown that the carbonaceous component, is responsible for much of the aerosol optical depth [*Hegg et al.*, 1997]. A persistent haze layer was discovered over most of the Indian Ocean in the winter during the Indian Ocean Experiment (INDOEX). [*Ramanathan*, 1999] This layer, a complex mix of organics, black carbon, sulfates, nitrates, and other species, subjected the lower atmosphere to a strong radiative heating and to a larger reduction in the solar heating of the ocean. They reported that BC contributed only 10% to the visible optical depth, but dominated the surface forcing.

Aerosol and cloud particles are important in tropospheric chemistry particularly in their effect on the sulfur and nitrogen cycles relevant to ozone photochemistry. Tropospheric ozone is an important secondary pollutant that can be damaging to vegetation and is a potential health hazard. It is an important "greenhouse" gas and photolysis of ozone plays a key role in controlling tropospheric chemistry. [*Fehsenfeld et al.*, 1996] The chemical processes that determine the ozone distribution over the North Atlantic are accomplished by a sequence of gas phase and aqueous phase (cloud and precipitation) processes. Species important to ozone photochemistry, particularly organics, can be scavenged by aerosol and cloud particles or can nucleate to form new particles. In addition, aerosols can absorb UV radiation important to photochemistry. *Buhr et al.* [1996] observed strong correlations among O_3, CO, NO_y, and aerosols at altitudes below 1500 m. The ratio of aerosol concentrations to O_3 was found to provide a

measure of the photochemical age of the air mass, similar to the NOy to O_3 ratio, suggesting a linkage between ozone photochemistry and heterogeneous processes. [*Buhr et al.*, 1996] Based on surface measurements made during NARE 1993, *Liu et al.* [1996] showed that cloud processing activated particles via S(IV) oxidation in marine stratus. They associated non-sea salt sulfate ions and ammonia ions with the scavenging of H_2SO_4 to particles with diameters > 200 nm. Organic ions, predominantly oxalate, were associated with CCN with diameters < 400 nm suggesting gas-to-particle conversion.

2.2 Objectives

We propose to characterize and understand the physiochemical properties of the aerosols in the anthropogenically-modified atmosphere of Eastern Asia and the Northwest Pacific and to study their relevance for radiative forcing of climate. We propose to accomplish this by characterizing the composition and composition-specific size distribution of aerosol emanating from the Asian continent during the ACE-Asia intensive field study. We will use an instrument that employs both thermal volatilization and evolved gas (TV/EG) analyses. This will allow us to make an in situ, real time, and artifact free determination of the relative contributions of sulfate, nitrate, sea-salt, organic species, and elemental carbon that make up the aerosol. This instrument is described in detail in section 2.3. During the course of this proposal we will:

1. Conduct laboratory measurements of well-defined aerosol with the TV/EG instrument throughout the life of the project in order to determine the thermogram 'signature' of individual aerosol compositional groups.
2. Integrate and participate in the ACE-Asia intensive field study on the NOAA RV Ron Brown.
3. Conduct comparisons of our data with that from other instruments that measure aerosol physical and chemical properties.
4. Conduct closure experiments to assess the relevance of aerosol radiative forcing on climate. These closure experiments will be conducted using radiative transfers models to compare with other instruments, such as sunphotometers and satellites.

2.3 Overall Approach

A prerequisite for achieving a better understanding of the effects of aerosols on atmospheric chemistry, radiative transfer, and ultimately on climate is the capability of performing reliable airborne mass and number concentration measurements with adequate spatial resolution that can discriminate both carbonaceous (particularly organic) and inorganic aerosols. Conventional methods rely on filter-collected samples which suffer from several deficiencies. First, sampling artifacts greatly influence the composition of filter-collected organic material. Second, the volume of air sampled is by necessity small, often resulting in an amount of collected material that is insufficient for chemical analyses. Third, time resolution may be inadequate unless specialized sampling devices are used. It is therefore desirable to develop an approach that will give an artifact-free, essentially real time, measurement of mass and number concentrations of major inorganic and organic species.

Most field measurements of organic and inorganic aerosols to date are performed at surface level either from fixed ground based sites and, more recently, from ship borne platforms. Water-soluble inorganic species are commonly analyzed by ion chromatography. This technique is widely known and is not discussed here. These measurements involved filter or impactor sampling utilizing relatively long sampling times that are needed for collecting sufficient amounts of material for chemical analyses. Analyzing the inorganic components of such samples is routinely done with sufficient accuracy. However, analyzing the organic carbon content is a non-trivial problem even under favorable sampling

conditions. Uncertainties in BC and OC determinations by the commonly used methods have been demonstrated by an intercomparison study [Shah and Rau, 1990] which showed that most methods agree for total carbon (TC) but significantly differ for OC and BC determinations.

The proposed approach is based on the in-situ thermal volatilization analysis (TVA) combined with the ex-situ thermal evolved gas analysis (EGA) method. The problems with conventional approaches and the rationale for the proposed approach are described below.

2.3.1. The TV/EG instrument.

The ultimate goal of this proposal is to make in situ, real time, and artifact free determinations of organic and inorganic aerosol mass and number concentrations. This is accomplished by the TV/EG instrument which uses a combination of the Thermal Volatilization Analysis and Evolved Gas Analysis. In TVA, aerosol components (such as sulfuric acid, ammonium sulfate, and organic compounds) volatilize at some predetermined temperatures during passage through the heated inlet of the instrument. The volatilization results in a measurable stepwise decrease in a plot of the particle number concentrations versus temperature, called a thermogram. In EGA, filters that have been exposed to an aerosol-laden stream are subsequently analyzed in the laboratory. The carbon content of the aerosol is accurately measured as it evolves off the filters as a function of temperature. (Please see sections 2.3.3 and 2.3.4 for more complete descriptions of the techniques.) The TVA method provides in situ, artifact free characterization of aerosols, however, there is a trade off between temperature resolution (and therefore resolution of composition), temporal resolution, and cost. The EGA method provides excellent discrimination of aerosol OC and BC content, however, there are artifact and temporal sampling issues. Using the combined instrument to obtain thermograms for single-component aerosols in the laboratory pre- and post-mission, we will be able to validate the measurement capability of these techniques and better interpret the thermograms obtained in the field. TVA and EGA data have been compared in past campaigns, most notably ACE-2, TARFOX, and INDOEX. [cf. *Novakov* et al., 2000; *Novakov* et al., 1997; *Clark* et al., 1999] While these comparisons have led to significant findings, they have been limited by uncertainties in both techniques. A combined instrument, as we have proposed here, coupled with laboratory calibrations and comparisons can eliminate these uncertainties and provide for a more quantified characterization of the aerosol than has been possible in the past.

The proposed system, is shown schematically in Figure 1. Flow from a suitable inlet is ingested and split into four streams. The first is sampled at ambient conditions with a CNC, a filter set, a wire impactor, and an aethalometer. A filter set consists of a front and back quartz filter. The CNC measures total condensation particle number density. The wire impactor collects particles by impaction which can subsequently be analyzed with an electron microscope for size, morphology, and elemental composition. The aethalomoter measures total aerosol optical absorption. The other three streams are heated to different temperatures. Each stream is continuously sampled with a filter set. Each stream is alternately monitored by a CNC, Scanning Mobility Particle Sizer (SMPS), PCASP, and FSSP. The CNC measures the total number density of the aerosol after heating that can be compared directly to the measurement made in the unheated stream. The three sizing spectrometers give size distribution information over the size range from 0.01 to 20 μm. We expect that in some cases, the aerosol will have a mixed composition. In this case the total number density will not change but the size distribution will shift as various aerosol components are volatilized. Therefore, the size distributions are essential to characterizing the component makeup of the aerosol. The TSI SMPS sizes particles from 10 nm to about 800 nm. The PCASP is a Particle Measuring Systems probe that sizes particles between 100 nm and 3 μm. The FSSP is a Particle Measuring Systems probe that sizes particles between 3 and 20 μm. Both have been modified to work inside an aircraft or at a surface site. These instruments are similar to those proposed to measure ambient aerosol on the RV Ron Brown. This will facilitate comparisons of ambient aerosol size distributions and

composition-specific size distributions. The specifics of the instrument components are listed in Table 1. More information about these instrument components is available in the Appendix.

Table 1. Instrumentation Component Characteristics		
Instrument	Size Range	Comments
Quartz Filters	All sizes	Total and Organic Carbon
Ames Wire Impactors	0.010 – 3 μm	Morphology and elemental composition
DMA	0.010 – 0.8 μm	Composition-specific size distribution
PMS PCASP-100	0.10 - 3 μm	Composition-specific size distribution
PMS FSSP-300	0.3 - 20 μm	Composition-specific size distribution
Aethalometer	All sizes	Aerosol optical absorption

The real advantage to the TV/EG system is in its ability to measure number density and size distributions of each heated stream while simultaneously collecting filter samples for analysis with EGA. In the present system three temperatures are sampled in a sequential fashion. Each time that a heated airstream is sampled, a size distribution is obtained using the SMPS, the PCASP, and the FSSP yielding size distribution information from 0.01 to 20 μm. This allows not only the classification of the aerosol by its volatilization temperature but also the determination of the size distribution of that component of aerosol by comparison to the ambient size distribution. The combination of number density and size distributions will provide invaluable information on the character of the aerosol. Each heated stream will be continuously sampled with a filter set. At a given temperature, for example 250°C, we know that ammonium sulfate/bisulfate and some organics will volatize (see section 2.3.4 for details on the TVA). The CNC, SMPS, PCASP, and FSSP will only monitor the condensed species. The EGA (see section 2.3.3 for details on the EGA) gives a measure of the condensed organic material. By comparing the organic mass estimates from the EGA with the volume and mass estimates from the TVA we expect to be able to determine the amount of inorganic and organic material in the ambient aerosol. Further, our laboratory experiments will allow us to determine roughly the contribution of organic or inorganic aerosols.

A closure or check on the system will be made by comparison of results from heated streams with those from the ambient stream. The EGA yields total carbon and organic carbon content of the aerosol. From the organic carbon content, a value of organic mass can be estimated. Experience from INDOEX indicates that TVA is capable of estimating the BC/total mass ratio. [*Clarke*, 1999] This can then be compared with the EGA results.

Each heated stream is sampled at about a 5 min interval. This sampling time is dictated by the SMPS and should not present a problem considering the spatial scales encountered at the surface. The filters are changed out every 2 to 3 hours and the impactors can be changed out periodically, sampling typically for 10 min to 20 min intervals. It is relatively inexpensive to add additional heaters to the instrument but this must be weighted against its effect on temporal resolution, cost, weight, and power consumption. Ideally, one would like a CN counter to be dedicated to each heated stream in the system, however, to keep expenses down we have elected to go with the present system.

There are several reasons why we wish to measure particles in the coarse mode ($D_p>2\mu m$). Results from ACE-1 showed that supermicron aerosol were the dominant scatterers in the unpolluted marine boundary layer, while results from ACE-2 showed that submicron aerosol were the dominant scatterers in a polluted environment [*Quinn* et al., 2000]. Also, single-particle analysis on Asian dust found that 50 to 80% of the large particles ($D_p>2\mu m$) were coasted with sulfate [*Parungo* et al, 1995]. Finally, results from filter analysis during ACE-2 show that a substantial amount of OC and BC are present in the supermicron particles [*Novakov* et al., 2000]. We feel that it will be very important to include measurements of these particles especially when performing closure experiments as outlined below.

2.3.2. Laboratory Characterization.

We will perform laboratory experiments prior to and after the ACE-Asia field study with the TV/EG instrument with the objectives of
1. obtaining the 'fingerprints' of OC, BC, and inorganics in the TVA and EGA thermograms,
2. conducting intercomparisons between the thermal volatilization and evolved gas techniques,
3. determining the appropriate conversion from carbon content to carbon mass, and
4. determining the appropriate trade-offs between species specification and temporal resolution with the TVA method.

Thermograms from the EGA and TVA are shown in Figures 2 and 3 and are discussed in subsequent sections. In the laboratory, TVA thermograms are constructed by ramping the temperature. Laboratory experiments using single-component organic aerosols will be performed while simultaneously collecting aerosol samples from the heated stream on filters. Thermograms from both EGA and TVA for these single-component aerosols can be compared to eliminate or reduce the uncertainties of the field measurements. These signatures will also be used to help us interpret the data we acquire in the field.

Wolff et al. (1991) suggested that OC values should be multiplied by a factor of 1.5 for calculation of the total organic mass associated with the OC, but various investigators have used values of 1.2 to 1.6. One object of the laboratory experiments will be to explore the correct value of this factor that is applicable to Asian outflow events. These laboratory studies will continue throughout the life of the proposal.

During SONEX, the NASA/ARC TVA instrument used temperature cuts of 120°C, 200°C, and 300°C as the characteristic temperatures for the volatilization of sulfuric acid, ammonium sulfate, and refractory particles, respectively. During INDOEX it was discovered that organics carbon tended to evolve at temperatures below 380°C while black carbon tended to evolve at temperatures greater than 380°C in an oxygen environment used in the EGA. One goal of our laboratory experiments will be to determine the temperature cutoffs that will be used during ACE-Asia. The capability of the heaters allows for temperatures greater than 500°C. Measurements made at appropriate temperatures can be used for comparison of the two techniques. The temperatures selected for any particular experiment will depend upon the species one is interested in discriminating.

2.3.3. Filter sampling and Evolved Gas Analysis.

Both analytical and sampling artifacts cause uncertainties in OC determination from filter-collected samples. Sampling artifacts are caused by the presence of both particulate and gaseous organic species in the air sampled through a fibrous filter material such as quartz, the preferred filtration medium for carbonaceous aerosols. Because some gaseous species may adsorb on the filter, the carbon concentration retained on the filter is the sum of particulate and adsorbed species. If unaccounted for, this sampling artifact (referred to as the 'positive' artifact) will result in an overestimation of organic aerosol

mass concentrations [*McDow and Huntzicker,* 1990; *Fitz*, 1990]. Furthermore, aerosol particles may contain semivolatile organic species, which may be desorbed from the particulate phase during sampling [*Eatough et al.* 1993, 1996; *Novakov et al.*, 1997]. This 'negative' artifact may lead to underestimates of the total organic aerosol mass concentration. Although the effects of these artifacts can be relatively well quantified this requires the use of elaborate sampling and analytical procedures that are often precluded for practical reasons.

The carbonaceous material on the filters obtained in TARFOX, ACE-2, and INDOEX projects was characterized by the evolved gas analysis (EGA) method [*Novakov*, 1981, 1982], supplemented by the analyses of solvent extracted samples as outlined in *Novakov and Corrigan,* 1995. In this method, an aliquot of the collected sample is progressively heated at a constant rate in an oxygen atmosphere from room temperature to 600°C. The carbon-containing gases evolving from the sample as a result of volatilization, decomposition and combustion of the carbonaceous material are converted to CO_2 over a catalyst and monitored by a nondispersive infrared analyzer. A plot of the rate of carbon evolution versus temperature is called the thermogram of the sample. The area under the thermogram is equal to the total carbon (TC) content of the sample. Carbon thermograms show a structure, often in the form of well-defined peaks, indicative of the carbon-containing materials with different volatilization, decomposition and combustion properties. These can be deconvolved to derive the BC and OC concentrations.

Examples of thermograms obtained with the EGA technique collected during ACE-2 are shown in Figure 2. [taken from *Novakov* et al., 2000] A set of front and back quartz filters and an impactor foil are exposed to the aerosol-laden air. Supermicron particles are collected on the aluminum foil and submicron particles are collected on the quartz filters. The back filter, in theory, does not collect aerosol material. Differences in the thermograms of the impactor, font, and back filters provide a clue to the sampling artifacts and can be interpreted as follows. The thermogram of the front quartz filter shows two low temperature peaks at ~ 180°C and ~ 230°C and a larger and wider structure extending to 600°C. This later peak contains BC. Most of the carbon on the backup quartz filter is confined to a single peak at ~ 180°C coinciding with the most volatile peak seen with the front filter. In contrast, the impactor foil thermogram shows a broad structure extending from ~200°C to above 500°C, with a peak at ~ 480°C most likely due to BC. Absent are any low temperature peaks as seen on the quartz filters. This comparison suggests that the species giving rise to the 180°C peak, seen on both front and back filters, are gas phase organic species adsorbed on the quartz filter matrix. (Particles are not expected to penetrate the front filter.) Absence of volatile species in the foil thermogram is consistent with this suggestion because adsorption of gaseous organics is not favored on the low surface area impactor foil. Assuming that the positive artifacts dominate and all the carbon on the backup filter is caused by such artifacts, then the difference in the carbon loading on the front and back filters can be used to derive an approximate measure of total submicron aerosol carbon.

With appropriate laboratory analysis of known aerosol composition, a more definitive determination of the aerosol composition responsible for these peaks can be made. Such experiments are outlined in section 2.3.2.

2.3.4. Thermal Volatilization Analysis

The thermal volatility of ambient aerosol has been used in situ to investigate their physical chemistry. Earlier measurements used thermal volatility to look at changes in condensation nuclei [*Pueschel et al.*, 1973], aerosol light scattering [*Cobourn et al.*, 1978; *Larson et al.*, 1982], and chemical speciation [*Huntziker et al.*, 1977; *Clarke*, 1991; *Clarke et al.*, 1997]. In the TVA method, aerosols are characterized in situ by heating an aerosol-laden flow to different temperatures. The assumption behind the TVA is that certain aerosols (such as sulfuric acid, ammonium sulfate, sea salt, and organics) volatilize at prescribed temperatures during passage through the heated inlet of the instrument. Volatile

species removed during heating preferentially condense on the walls during subsequent cooling due to the high surface area of the walls relative to the remaining aerosol. The volatilization results in a measurable decrease of the particle number concentrations. The temperatures at which decreases in CN number concentrations occur give an indication of the species being volatilized. Examples of thermograms and size distributions measured in our aerosol labs at ARC and at LBNL are shown in Figures 3, 4, and 5. Figure 3 shows a thermogram and size distributions for an inorganic, ammonium sulfate. The number density decreases to about 30% between 180° C and 200° C, while the size distribution has shifted dramatically as the aerosol is heated. Figure 4 shows results for an aliphatic dicarboxylic acid, Oxalic Acid. Note that the number density at 300° C has only decreased to about 65%, the size distribution, however, has shifted dramatically as the aerosol is heated. Plotted in Figure 5 are results from another aliphatic dicarboxylic acid, Succinic Acid. Note the number density increases at a temperature of about 240° C. Note the gradual decrease in number density as a function of temperature as compared to Oxalic Acid in Figure 4. The size distribution has changed dramatically.

The TVA was used successfully by NASA/ARC during the recent SONEX mission. The instrument used three temperature thresholds to estimate the amount of sulfuric acid, ammonium sulfate/bisulfate and refractory particles in the air stream. The lower panel of Figure 6 [taken from *Ferry et al.*, 1999] shows the ultrafine particle concentration as a function of time obtained during SONEX. The upper panel of Figure 6 shows the fraction of CN that was volatilized after heating to 120˚C (indicated by diamonds) and that was left after heating to 300˚C (indicated by squares). Based on laboratory results such as Figure 3, the aerosol that volatilized after heating to 120˚C can be said to be sulfuric acid aerosol while that remaining after heating to 300˚C is considered refractory aerosol composed of dust, some species of OC, and BC. Since this method is only sensitive to aerosol, there are no artifacts as in the filter methods. By heating to higher temperatures we expect to be able to discriminate the refractory aerosol into compositional groups or families.

The TVA will be complicated by several issues. Volatilization temperatures for different species may be similar or within the uncertainties of our measurement. In this case we hope that comparison with the EGA will shed light on what the TVA is measuring. Our experience in SONEX showed that, in the upper troposphere, we could discriminate sulfuric acid aerosol from other aerosol in aircraft plumes. At lower altitudes it is likely that the aerosol will not be composed of purely one species. Preliminary results from INDOEX confirm that most aerosols are composed of a mixture species. Thus, as a particular species volatilizes, the total CN count does not decrease but the size distribution changes. Thus it is crucial that a measurement of size distribution be made as we have proposed here. Laboratory analysis of known aerosol composition will allow a more definitive determination of the aerosol composition. Such experiments are part of this proposal as described below.

2.3.5 Intercomparisons and Closure Studies

During FY 2001 we will continue to conduct laboratory experiments. Most of the year will be spent insuring that our instrument can integrate smoothly with the platform, conducting experiments during the ACE-Asia intensive field study, and making a quick analysis of our data. We are interested in comparing our data with other onboard instrumentation results, including water-soluble ion chromatography analysis, mass spectra analysis, on optical sensors such as sun photometers.

During the final year of funding we will make a final data analysis. Comparisons between the two techniques will be made. Comparison with other instruments, satellite, and model.

Determination of Size Dependent Speciation of the Aerosol. To the extent possible we will obtain the relative size-dependent contributions of sulfate, nitrate, organic aerosol, and elemental carbon to the total aerosol from our measurements and those of related instruments.

Closure Study of Aerosol Physical, Chemical and Optical Properties.

When an aerosol is subjected to a change in environmental conditions, such as being heated or cooled or being exposed to a higher or lower relative humidity, there is, in general a change in both its physical properties and its optical properties. In principle, the scattering humidification factor (f(RH)) can be measured, but there is currently no technique widely available to measure the absorption of an aerosol sample as a function of relative humidity. Frequently, for lack of better knowledge, the absorption humidification is assumed to be unity (meaning that there is no change in aerosol absorption due to an increase in ambient relative humidity). This assumption then enters the estimate of such particle optical properties as the single scattering albedo at ambient relative humidity, leading to erroneous results.

Modeling studies of the absorption humidification factor are being conducted at NASA/Ames Research Center[*Redemann*, et al., 1999]. Their basic model assumes that aerosols contain an insoluble BC (or soot) core and a coating, which determines hygroscopic growth behavior. The aerosol optical properties are then computed on the basis of a shell/core particle morphology using a Mie code for concentric shells. When an atmospheric aerosol particle collects a non-absorbing shell, the core is exposed to an increased electric field and this can increase the specific absorption of the soot particle. Preliminary modeling studies show that the absorption of an atmospheric aerosol particle composed of a soot core and an aqueous sulfuric acid shell may increase by a factor of about 50 percent when the relative humidity changes from 30 to 95%. This increased absorption is a function of the initial particle size and the soot mass fraction. *Redemann* et al. [1999] have estimated that the difference in the wet and dry absorptions can lead to differences in single scattering albedo of about 0.03, depending on the details of the dry particle size distribution. For typical boundary layer size distributions the absorption humidification factors are small compared to the scattering humidification factors. As this work proceeds internally mixed aerosols of various types will be considered. Of particular interest is the identification of organic aerosols.

Calculations from the in situ measurements of size distribution and chemical composition made in this project can be compared to optical depth spectra measured by sunphotometers and satellites. Conversely, comparisons between size distributions retrieved from sunphotometer extinction or optical depth spectra and obtained from in situ measurements can also be made. We will study aerosol radiative effects over both land and ocean. Data from the new EOS Terra platform, launched December 18, 1999, will aid in this regard. Terra carries the sensors Moderate-resolution Imaging Spectroradiometer (MODIS), Multi-angle Imaging Spectro-Radiometer (MISR), Measurements of Pollution in the Troposphere (MOPITT). The multi-angle measurements of MISR, and the improved spectral resolution of both MODIS and MISR, will increase chances of accurate AOD retrievals over land. Sea-viewing Wide-Field-of-view Sensor (SeaWiFS) and MODIS data products will include aerosols in regions impacted by Asian continental outflow over both the Pacific and Indian Oceans, with and without coastal stratus.

2.4 Relationship of the Proposed Research to ACE-Asia Goals

The goals of ACE-Asia are to determine and understand the properties and controlling factors of the aerosol in the anthropogenically modified atmosphere of Eastern Asia and the Northwest Pacific and to assess their relevance for radiative forcing of climate. To achieve these goals, ACE-Asia scientists will pursue three specific objectives:

Objective 1. Determine the physical, chemical, and optical properties of the major aerosol types in the Asian Pacific region, determine its state of mixing, and investigate the relationships among these properties.

Objective 2. Quantify the physical and chemical processes controlling the evolution of aerosols in the Asian Pacific region and in particular their physical, chemical, and optical properties.

Objective 3. Evaluate numerical models which will extrapolate aerosol properties and processes from local to regional and hemispheric scales, and assess the regional direct and indirect radiative forcing by aerosols in the Asian Pacific region.

In order to address these goals, the AA-SEC outlines three groups of questions. We feel that this proposal is capable of contributing to all of the following questions:

Aerosol Survey

What are the vertical and regional distributions of aerosol concentrations and properties under various meteorological conditions?

A. *What are the relative size-dependent contributions of sulfate, nitrate, carbonaceous material, sea salt, primary anthropogenic particles, and dust to the optical properties (absorption, total and angular scattering) of aerosols?*

The TV/EG instrument is specifically designed to measure the size-dependent contributions of sulfate, nitrate, carbonaceous material, sea salt, primary anthropogenic particles, and dust to the total aerosol. Combining these measurements with computer simulations of Mie scattering theory will provide estimates of the optical properties of the aerosol. The relative contribution of primary and secondary sources to the total organic content of atmospheric aerosol is largely unknown. Since OC plays such a major role in the uptake of water by particles, climate models need more specific information in order to treat organic matter more realistically and hence predict radiative forcing by aerosols more realistically.

B. *How do the interactions between these species (their state of mixing) affect their optical properties?*

Optical properties of condensed species are not dependent on their composition but on their state of mixing, eg. , whether they are externally or internally mixed; is the absorbing portion of the aerosol mixed in the center or side or evenly distributed throughout the aerosol. We hope to gain insight into this issue from our species-specific size distributions, Mie calculations, comparisons with instruments that measure the gross optical properties of the aerosol in the atmosphere such as the Ames Airborne Tracking Sunphotometer (Proposal GC00-277) or similar instrument.

C. *How are the distributions affected by specific meteorological events?*

Our measurements combined with other measurements and trajectory calculations can help to answer this question. We can assess how the ratio of carbonaceous to non-sea salt mass changes with time and conditions in the Asian plume. One of the principal results of TARFOX was that levels of organics aloft exceeded those at the surface (Novakov et al., 1997). Few measurements exist that enable us to generalize or explain this finding. ACE-Asia provides an opportunity to pursue this issue.

Aerosol Interactions with Gas-Phase Atmospheric Chemistry

What role does the atmospheric chemistry of the Asian-Pacific region play in influencing aerosol properties and evolution, and likewise, how does the Asian aerosol affect tropospheric chemistry in the region?

D. *How does mineral dust interact with atmospheric gas-phase chemistry?*
E. *How does sea salt interact with gas-phase chemistry?*
F. *How does the anthropogenic/urban aerosol interact with gas-phase chemistry?*

The impact on the size distribution of homogeneous oxidation by OH (Cox & Shepard, 1980), in-cloud oxidation by peroxide (*Penkett* et al., 1979), and sea-salt oxidation by ozone (Sievering et al., 1992) are all very different. Only the first can nucleate new particles and create accumulation mode sulfate. Do the relatively high levels of ammonia in Asian air (Zhao and Arpu, 1994) change the relative reaction rates by raising the pH? Observations are lacking to constrain models of these processes over the northwestern Pacific.

Of the Measurement listed in Table 2. of the AA-SEC (Huebert et al, 1999) entitle Measurement Priorities, we meet 5 measurement categories, Speciated Organics, Size-Resolved Organics (EC/OC), and Aerosol Physical Size Distribution in the Aitken, Accumulation, and Coarse Modes. The preponderance of these measurements are listed as essential in both the aircraft and ship measurement categories, and as essential in responding to all nine science questions listed above.

Chemical transport and radiative transfer models generally treat the tropospheric aerosol as several separate components: often mineral dust, black carbon, organic carbon, sulfate, industrial aerosol, and sea-salt. The interaction between these species can affect their optical properties. Results from ACE 1 have shown that the atmospheric aerosol, even in remote regions, is rarely present as a pure chemical external mixture in any size range. In the ACE 1 study area, between 11 and 46% of the sulfate particles with diameters > 100 nm contained soot (Postfai et al., 1999). Organic species were detected in over 50% of the particle with diameters > 160 nm and were associated with sea-salt (Middlebrook et al., 1998). Over 90% of the aerosol particles with diameters > 130 nm contained sea salt (Murphy et al., 1998). The degree of mixing of the various chemical species has a major effect on the optical properties of the aerosol. The presence of less soluble organic species will alter a particle's hygroscopic properties (Zhang et al., 1993). Similarly, mixing with soot will increase light absorption and decrease the solubility of sulfate particles.

These compositional changes can have a profound effect on single scatter albedo, ω, and refractive index, *m*. *Bergstrom and Russell* (1999) used the AVHRR/NOAA AODs reported by *Husar et al.* [1997] for the period July 1989-June 1991 in combination with aerosol intensive properties determined primarily in TARFOX to calculate the aerosol-induced change in net shortwave flux at the tropopause. They showed that changing ω from 0.9 to 1.0, while keeping AOD and all other properties unchanged, increased the computed annual regional average flux change by 37% (from -3.5 to -4.8 W m^{-2}).

Changing aerosol complex refractive index *m* to change ω can produce even larger changes in the aerosol scattering phase function at satellite view angles. For example, *Stowe et al.* (1997) report that increasing m_i from 0 to 0.01 in the model of *Ignatov et al.* (1995) decreased ω by only 10% while simultaneously decreasing the scattering phase function by ~30%, thus decreasing their product by ~37% and increasing aerosol optical depth derived from satellite measurements by ~59%.

2.5 Proposed Tasks

2.5.1 Year One, FY 2000.

Task 1.1: Purchase and Integration of Additional Heater and CNC. Our current laboratory set up uses one heater which we cycle through different temperatures to obtain thermograms. While this is adequate for laboratory operation, it is desirable to have dedicated heaters for each temperature regime and this is what is proposed. We wish to purchase these heaters early to allow for the automation of the heating system and to insure flawless operation. It is absolutely essential that the ambient stream be continuously monitored by a CNC, therefore we will purchase this device and integrate it into our instrument at the earliest possible time.

Task 1.2: Laboratory Experiments. As detailed in sec. 2.3.2, extensive laboratory tests will be conducted on controlled aerosol samples to determine to the greatest extent possible what the appearance of thermograms for various inorganic, organic, and elemental carbon aerosols. The protocol by which we will compare EGA and TVA results will be perfected during this period. Samples from clean and polluted air will also be taken at selected sites around the San Francisco Bay area during this time.

2.5.2 Year Two, FY 2001

Task 2.1: Integration on the RV R.H. Brown.
Task 2.2: Pre-Mission Calibration. All of the components of our combined instrument will be calibrated prior to the mission. This includes the flowmeters, CNC's, DMA, PCASP, and FSSP. Some of these calibration will be conduced in our labs and some equipment must be sent to the manufacturer.
Task 2.3: TV/EG Instrument Measurement During ACE-Asia Intensive Field Study.
Task 2.4: Post-Mission Calibration. To insure the highest data quality, post calibration of the instrument components is required.
Task 2.5: Preliminary Analysis of Data Products.

2.5.3 Year Three, FY 2002

Task 3.1: Intercomparisons, Validations, and Integrated Closure Analyses. The intercomparisons, and closure studies outlined in sec. 2.3.5 will be conducted. Data will be exchanged, archived, and released to the scientific community according to ACE-Asia protocols (Huebert et al., 1999b) and formats.
Task 3.2: Laboratory Experiments. It is likely that some of the data collected during the intensive field study will not be interpretable based on pre-mission lab tests. It will therefore be necessary to conduct post-mission tests to aid in the interpretation of these data.

2.6 Schedule

2000   Integration planning on the RV R.H. Brown (~Aug)
        Laboratory Experiments (May-Dec)
        ACE-Asia Science Team Meeting, Hawaii (Fall)
        Intensive Field Study Planning Meeting, Iwakuni Marine Base, Japan (~Sep/Oct)

2001   Pre-mission instrument calibration (Feb)
        Transit from Hawaii to Japan (Mar)
        ACE-Asia intensive deployment, Iwakuni Marine Base, Japan (25 Mar-30 Apr)
        Post-mission instrument calibration, (May)
        Data reduction and initial closure tests (May-Dec)
        ACE-Asia Science Team Meeting and Data Workshop (~Oct?)
        ACE-Asia Special Session at Scientific Conference (primarily individual analyses; ~Dec?)

2002   Update optical models using ACE-Asia results (Jan-Aug)
        Continuing closure studies (Jan-Dec)
        ACE-Asia Special Session at Scientific Conference (including integrated analyses; ~May?)
        ACE-Asia Science Team Meeting and Data Workshop (~Sep?)
        ACE-Asia Special Journal Issues

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3. BUDGET AND REQUIREMENTS

Budget
>   The budget for this investigation is included on the pages 17. During the first year we will need to purchase a TSI 3025A CN Counter, heaters, and valves to complete our system. We wish to do this as early as possible to insure that the components function properly. The second year's budget includes instrument calibrations and electronic upgrades for the FSSP and PCASP. The budget also includes a share of the procurement of an appropriate inlet and aerosol container for integration onto the RV Ron Brown. We feel that the manpower requests are adequate to perform the work outlined in this proposal. The cost of a part-time contractor who will assist in data analysis and closure studies is included in the third year of funding.
>   ARC program Support provides institutional funds for center infrastructure and although a direct cost in this budget, should be considered as the equivalent to the university requirement for indirect cost.

Integration Requirements
>   Our instrument is designed to measure aerosol particles in the size range from 0.01 to 20 μm. Thus it will need to be located near the bow. Integration issues have been discussed with Dr. Tim Bates and the budget reflects construction of an additional aerosol container and inlet. Volumetric flow rates required are 36 Liters per min. The instrument is 2' high x 2' wide x 5' long and is supported by an instrument rack that is 4' high x 2' wide x 2' deep. It weighs about 250 pounds and draws 30 Amps at 120 Volts.

Hazardous substances.
>   The instrument uses Butanol.

Transportation Requirements
>   The budget assumes that UCAR/JOSS will cover the transportations costs associated with integration and deployment. Two people are required for integration onto the ship. One scientist will transit from Hi to Japan, the other will return home. The person onboard ship will be replaced in Japan by a scientist who will remain onboard for the duration of the experiment. Another person will be required to help download equipment. This information is listed below. The dates are approximate.
>> Travel for one person from San Francisco to Hawaii for integration on Mar. 3, remain in Hawaii for 7 days, return Mar. 10.
>> Travel for one person from San Francisco to Hawaii for integration on Mar. 3, remain in Hawaii for 7 days, travel onboard RV to Japan, return from Japan to San Francisco on Apr.1.
>> Travel for one person from San Francisco to Japan on Mar. 31, deploy with RV, return on Apr. 30.
>> Travel for one person from San Francisco to Japan for download on Apr. 30, return on May 3.

4. CURRENT AND PENDING SUPPORT

5. MANAGEMENT APPROACH AND PERSONNEL

Overall project management, administration, and communications with NOAA Headquarters will reside with the Principal Investigator, Dr. A. W. Strawa. A cooperative agreement will be established between NASA/Ames Research Center and Lawrence Berkeley Laboratory to accommodate administrative and budgetary details and to facilitate research collaboration. The Aerosol Groups at ARC and LBL have been collaborating informally for the past 6 months. The team assembled to conduct this investigation has broad experience in the field. Scientific and managerial responsibilities are outlined in Table 2.

Formal, annual project reviews will provide NOAA program management with detailed summaries of current research plans. Our intention is to keep the relevant parties in NOAA informed of our results as soon as they become available. Reporting to the scientific community will be accomplished by presentation of results at one or more scientific meetings per year, as well as at least one journal publication annually.

All facilities needed for this investigation are currently available at ARC and LBL. In this proposal, two groups with long and successful track records in airborne measurements join to focus on one of the most difficult problems of particle measurement: quantitative characterization of the composition of aerosol and cloud particles.

Table 2. Investigator Responsibilities

| Investigator	Role	Responsibility
Dr. A. W. Strawa	Principal Investigator	•Overall scientific direction, project management, administration, and communications with NOAA. •Laboratory experiments with TVA. •Construction and deployment of combined aircraft instrument.
Dr. T. Novakov	Co-Investigator	•EGA analysis. •Interpretation of thermograms •Scientific interpretation of results.
Dr. R. F. Pueschel	Co-Investigator	•Provide particle measurement expertise. •Analysis of data from PCASP, FSSP, and AWI as required. •Assist with scientific interpretation of results and aircraft integration.
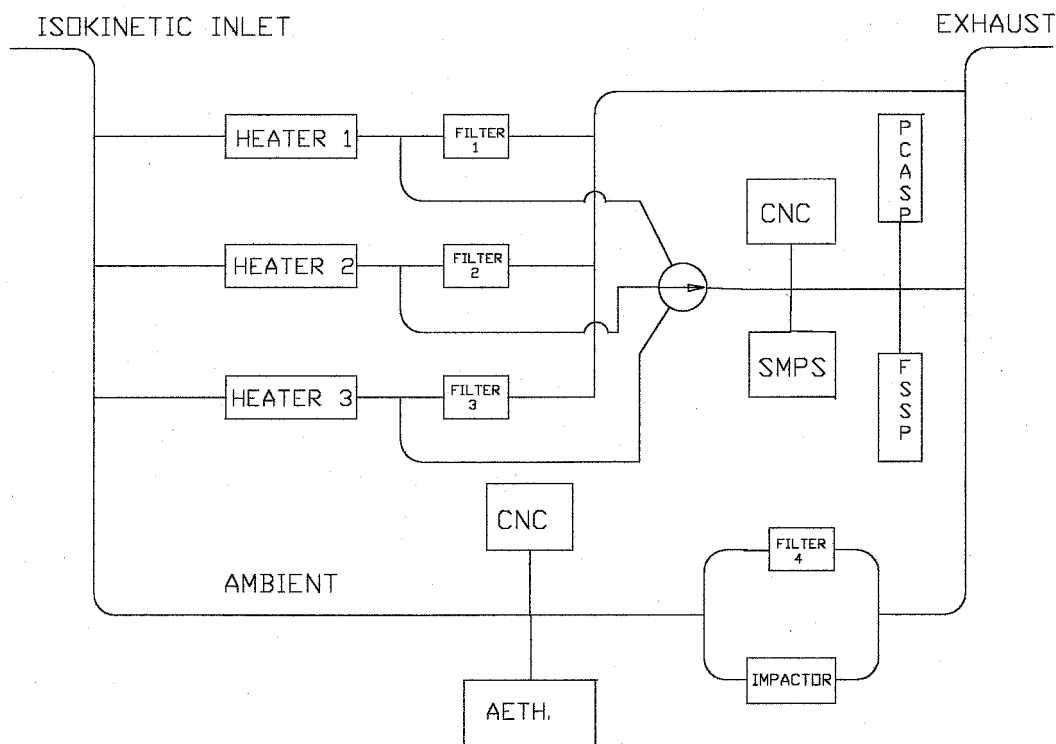
Figure 1. Schematic of TV/EG Instrument. Flow from a suitable inlet is ingested and split into four streams. The first is sampled at ambient conditions with a CNC, a filter set, a wire impactor, and an aethalometer. A filter set consists of a front and back quartz filter. The CNC measures total condensation particle number density. The wire impactor collects particles by impaction which can subsequently be analyzed with an electron microscope for size, morphology, and elemental composition. The aethalomoter measures total aerosol optical absorption. The other three streams are heated to different temperatures. Each stream is continuously sampled with a filter set. Each stream is alternately monitored by a CNC, Scanning Mobility Particle Sizer (SMPS), PCASP, and FSSP. The three sizing spectrometers give size distribution information over the size range from 0.01 to 20 μm. See sec 2.3.1 for more details.
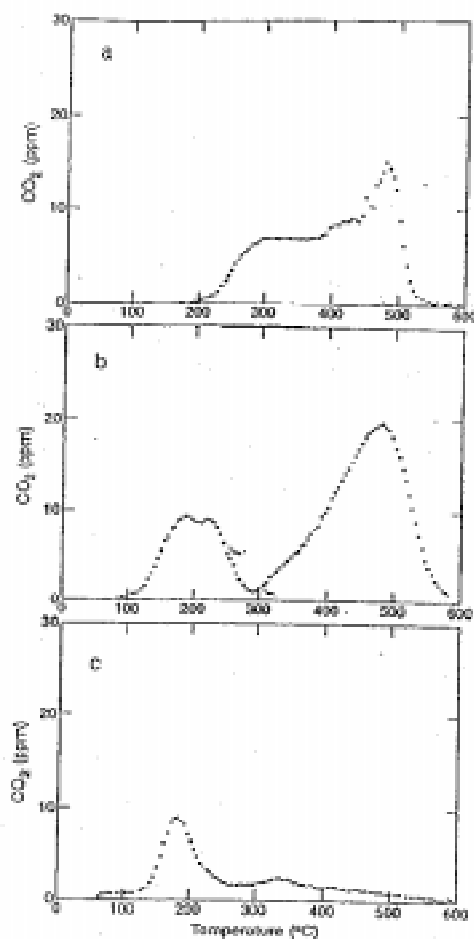
18

Fig. 2. Examples of ECA thermograms of (a) super-micron particles collected on impactor foils, (b) sub-micron particles collected on front filter and (c) adsorbed gas-phase species collected on backup filter (sample set 12).
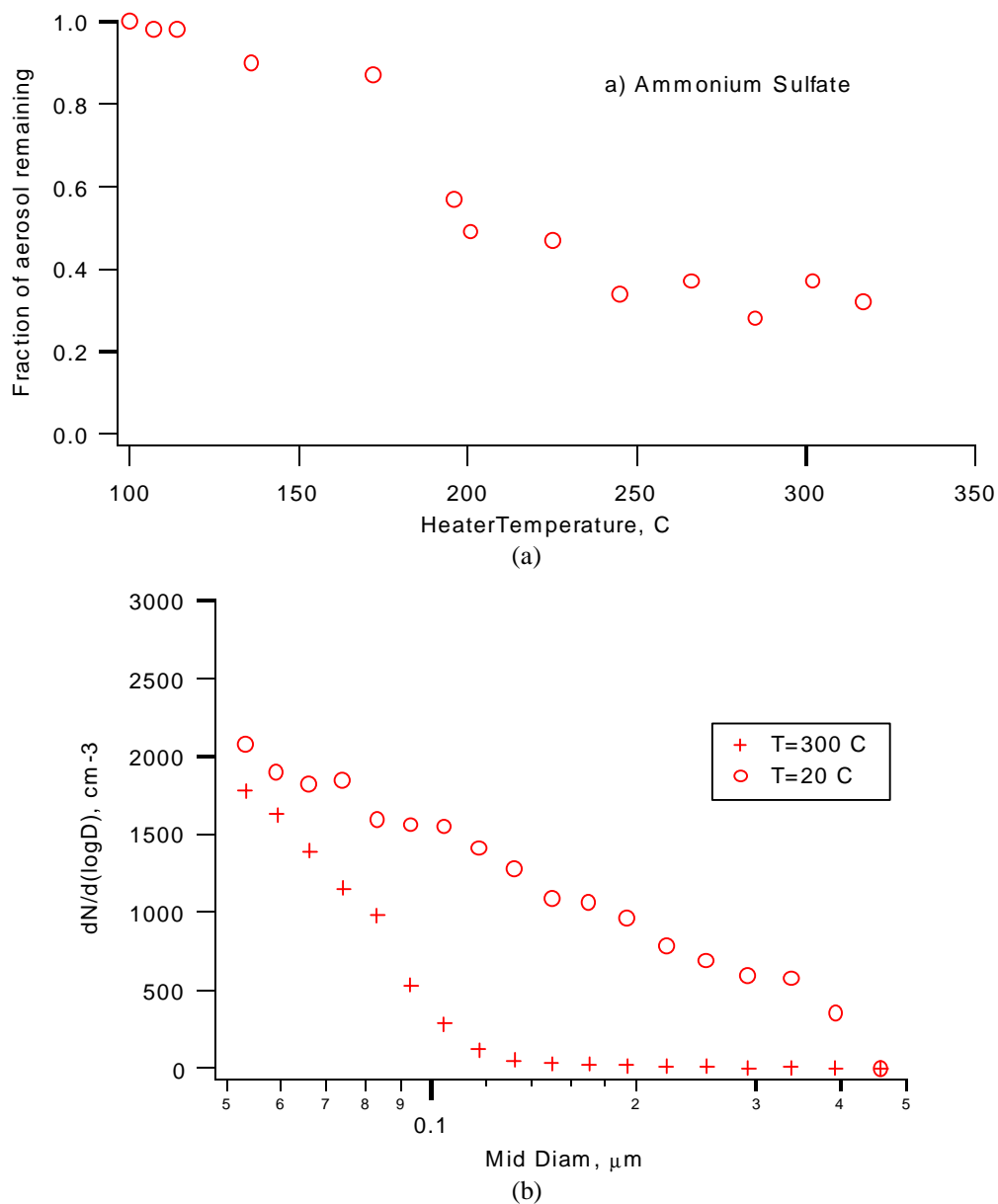
Figure 3. TVA Results for Ammonium Sulfate. a) a) Fraction of Ammonium Sulfate aerosol remaining as a function of heater temperature in the TVA instrument. b) Comparison of size distributions for Ammonium Sulfate aerosol at ambient conditions, 20° C, and heated, 300° C. The number density decreases to about 30% between 180° C and 200° C, while the size distribution has shifted dramatically as the aerosol is heated.
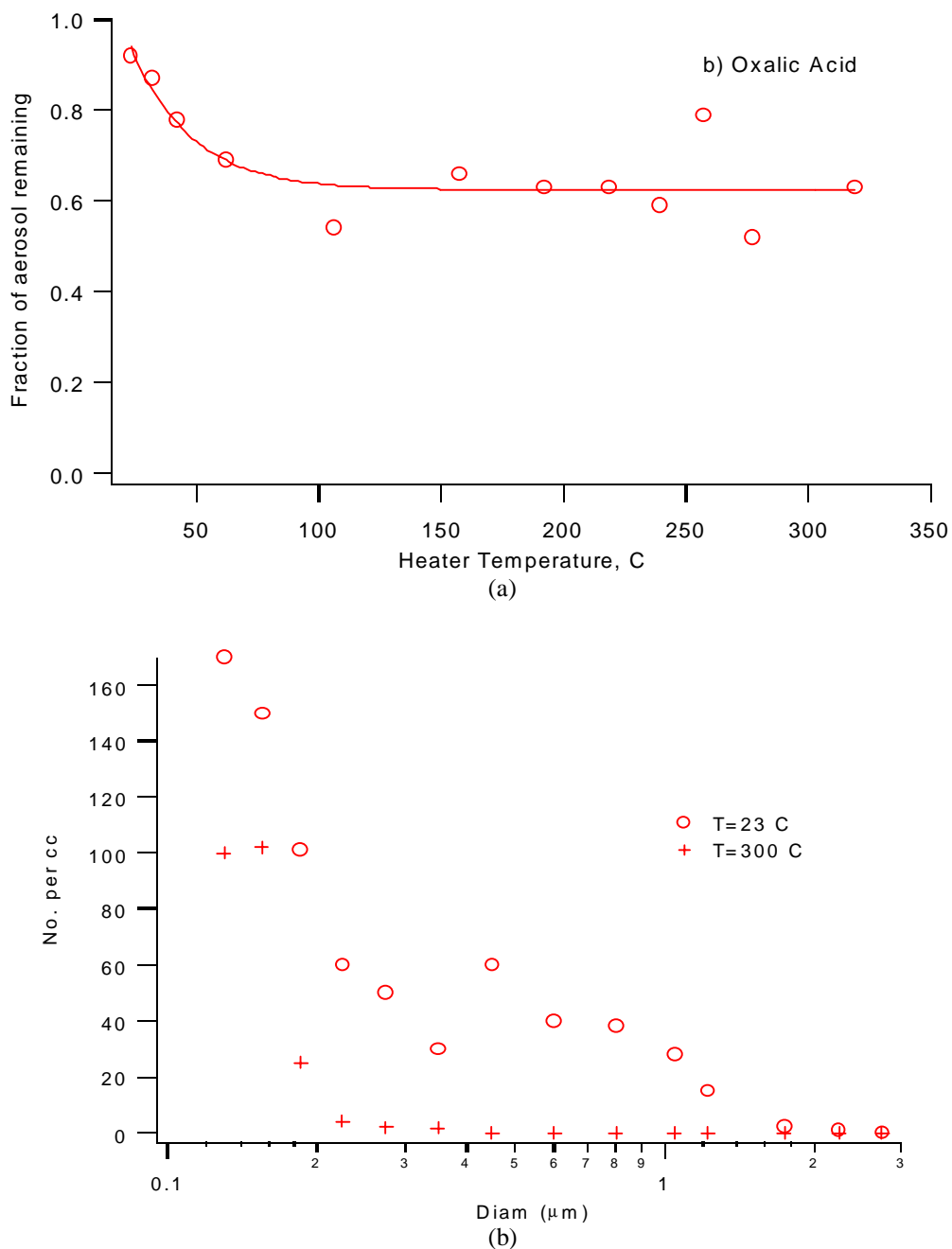
Figure 4. TVA Results for Oxalic Acid. a) Fraction of Oxalic Acid aerosol remaining as a function of heater temperature in the TVA instrument. b) Comparison of size distributions for Oxalic Acid aerosol at ambient conditions, 23° C, and heated, 300° C. While the number density at 300° C has only decreased to about 65%, the size distribution has shifted dramatically as the aerosol is heated.
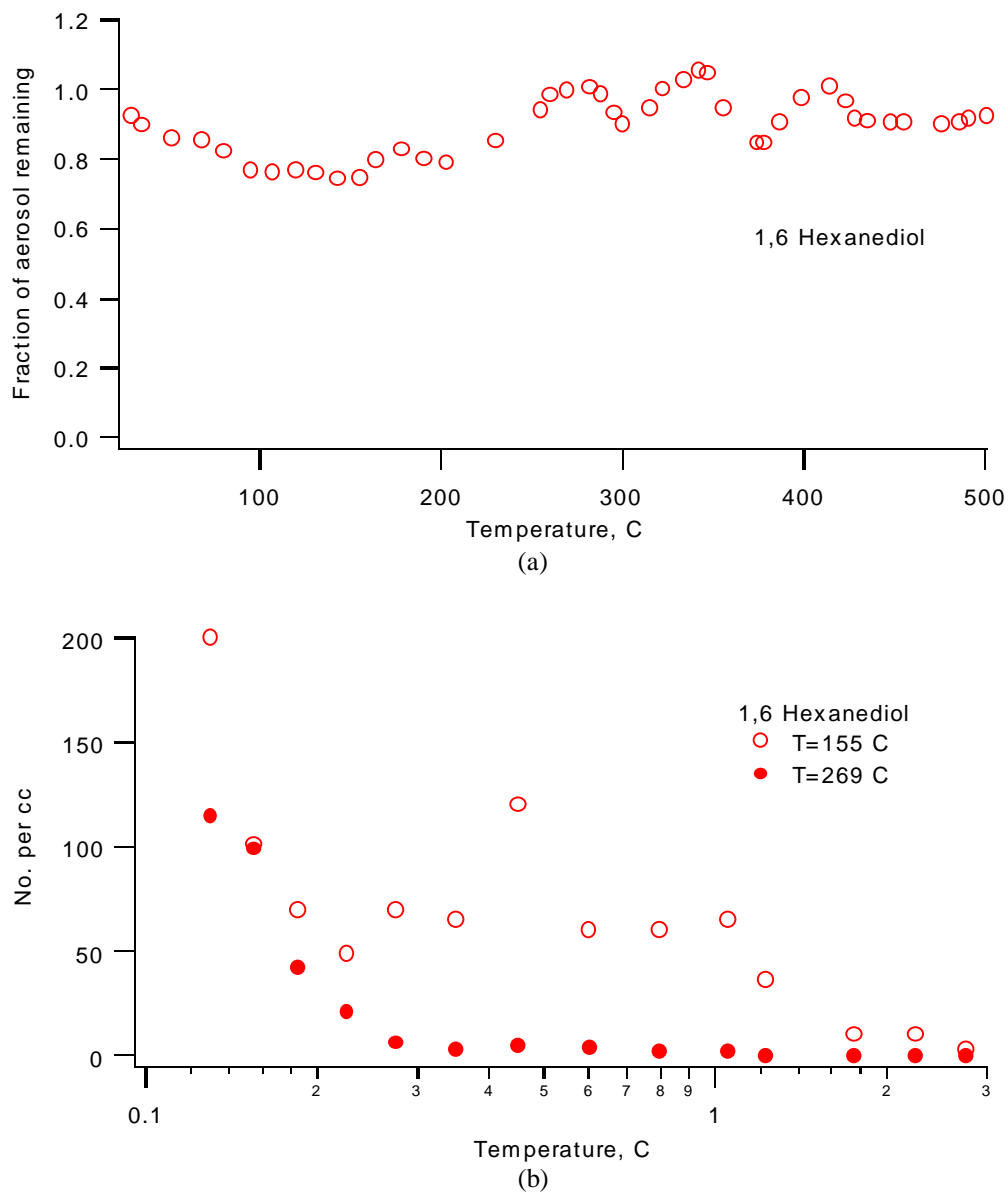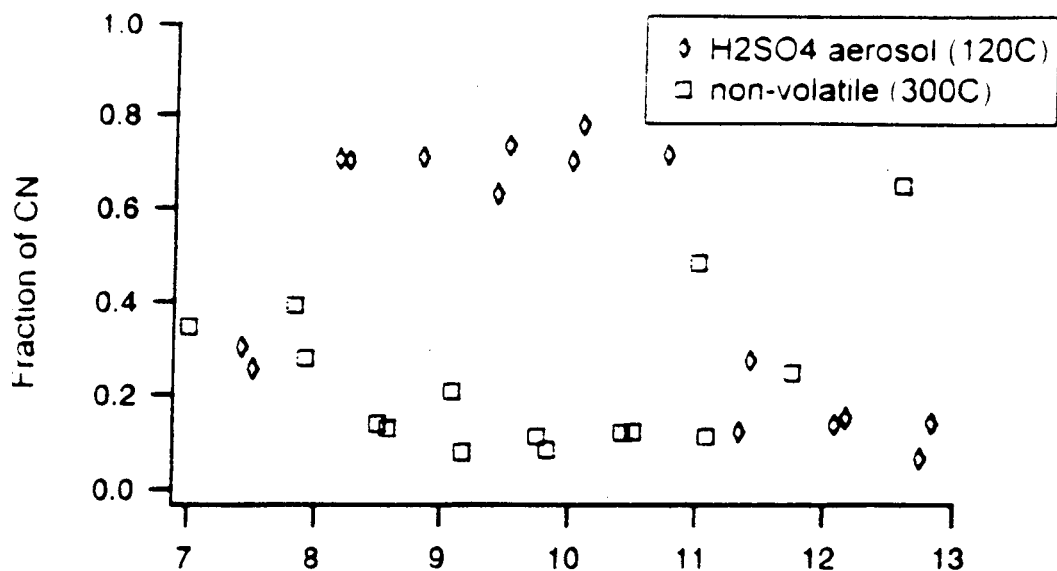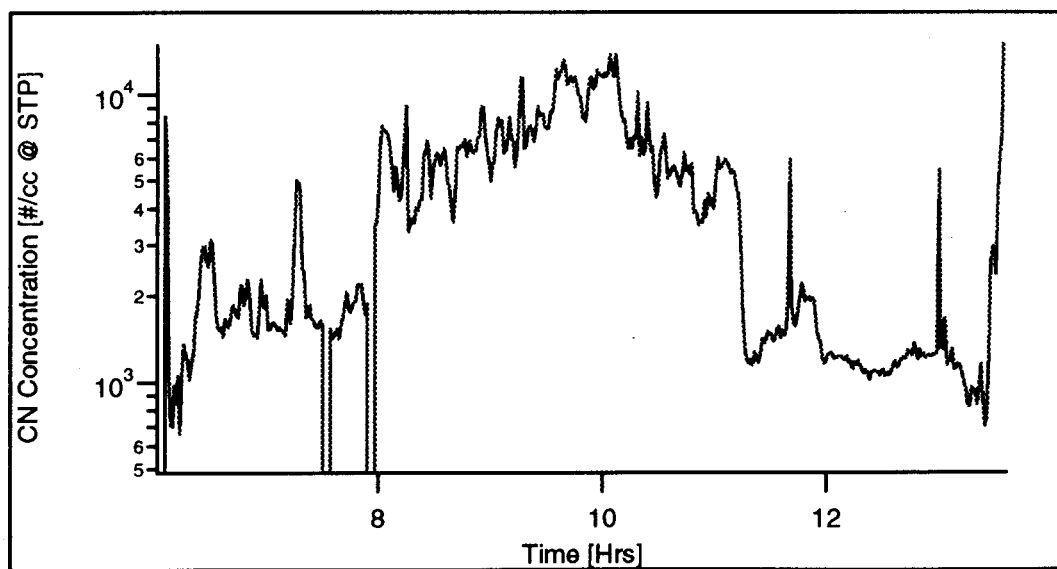
(a)

(b)

Figure 5. TVA Results for 1,6 Hexanediol. a) Fraction of Hexanediol aerosol remaining as a function of heater temperature in the TVA instrument. b) Comparison of size distributions for Hexanediol aerosol at low temperature, 155° C, and heated, 269° C. Note the number density increases at a temperature of about 240° C. At this temperature the size distribution shifts.

a

b

Figure 6. Measured CN during SONEX 23 Oct. 1997.
a)Fraction of CN atributed to sulfuric acid aerosol and refractory aerosol.
b) Total CN.

APPENDIX: BRIEF DESCRIPTION OF INSTRUMENT COMPONENTS

Scanning Mobility Particle Sizer (SMPS)

Size distributions will be measured using a Scanning Mobility Particle Sizer (SMPS) that incorporates a differential mobility analyzer (DMA), a condensation particle counter (CPC), and data acquisition/analysis software. The DMA uses electrical mobility to separate particles of different size and produces an output aerosol of uniform size. The CPC counts particles by condensing supersaturated butanol vapor onto all particles larger than 3 nm. The particles spontaneously grow to large size and are then detected optically. The SMPS uses the DMA to extract a monodisperse aerosol from a polydisperse, source aerosol and then measures the number in that size bin using the CPC. The computer correlates the scanned particle sizes with the CPC counts and calculates the size distribution of the sampled aerosol. The apparatus is capable of measuring size distributions in the range of 10 nm to 600 nm and takes between 3-5 minutes for a complete scan.

Passive Cavity Aerosol Spectrometer Probe (PCASP)

In the PCASP particle from 0.1 to 3.0 μm diameter are sized by passing through the cavity of a HeNe laser. Light is collected from 35 to 120 degrees ad focused onto a photodiode by a parabolic mirror. The electronic response is a function of particle size via an instrument response curve established by instrument calibration. Time resolution is one size distribution per second.

Forward Scattering Spectrometer Probe (FSSP)

The FSSP measures particles between 0.5 and 20 mm diameter. The particles pass through a HeNe beam. In this instrument, the light scattered from a particle in the forward lobe (from 7 to 11 degrees) is collected onto a photodiode. The electronic response is a function of particle size via an instrument response curve established by instrument calibration. Time resolution is one size distribution per second.

Aethalometer

An aethalometer measures the extinction, or attenuation, of a beam of light transmitted through a quartz filter while sample air is continuously drawn through the filter. Light attenuation in the atmosphere is due to both absorption and scattering by gases and particles. Inside the optical cell of the aethalometer, the dominant factor is the absorption by particles, and black carbon is the principal light absorbing component of atmospheric particulate matter. Consequently, the measurement of optical attenuation by the aethalometer can be used to infer the concentration of black carbon particles in the sampled air. *Gundel et al.* (1984) have shown that black carbon (BC) concentration and light attenuation are linearly correlated. Calibration of the aethalometer involves independent determination of BC concentration in order to estimate the value of the attenuation coefficient. Since the light absorption technique is non-destructive, the filter samples collected in the aethalometer can be used for subsequent chemical analysis of BC content. The evolved gas analysis (EGA) method described in section 2.3.3 will be used for this purpose.

Ames Wire Impactors (AWI)

The AWI was developed at Ames and have been deployed frequently on both the ER-2, DC-8, and unpilotted aircraft. It has proven to be an accurate and reliable means for obtaining aerosol size distribution, morphology and elemental composition. Thin Palladium wires (500 μm diameter), and filters, are exposed to an aerosol laden airstream. Submicron particles stick to the wire upon impact by virtue of Van de Waals forces. The wires are returned to the laboratory for aize and shape analysis with a scanning or transmission electron microscope and for elemental composition measurements by X-ray dispersive analysis.